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APPLICATION FOR LETTERS PATENT

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**METHODS OF FORMING INSULATING
MATERIALS**

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Methods of Forming Insulating Materials

TECHNICAL FIELD

The invention pertains to methods of forming insulating materials, such as, for example, materials comprising silicon oxide. In exemplary applications, the invention pertains to methods of forming boron and/or phosphorous doped materials comprising fluorine, silicon and oxygen.

BACKGROUND OF THE INVENTION

Silicon oxide materials (such as, for example, silicon dioxide) are commonly used in semiconductor device fabrication as insulating materials. Silicon oxide materials can be formed by chemical vapor deposition (CVD) from appropriate precursors. An exemplary combination of precursors that can be utilized for forming silicon oxide materials is silane (SiH_4) and hydrogen peroxide (H_2O_2). Another precursor combination which can be utilized for forming silicon oxides is tetraethyl orthosilicate (TEOS) and ozone (O_3).

Silicon oxide materials can be doped with one or both of boron and phosphorous to alter (lower) a dielectric constant of the material. The boron and/or phosphorous can be introduced into a silicon oxide material by, for example providing one or both of a boron-containing precursor material and a phosphorous precursor material in a CVD reaction chamber during deposition of the silicon oxide material.

1 Suitable phosphorous precursor materials include, for example, PH_3 and
2 tetraethoxy phosphine (TEPO). Suitable boron-containing precursors
3 include, for example, B_2H_6 and triethyl borane (TEB). An alternative
4 method of introducing phosphorus and/or boron into a silicon oxide
5 material is to implant one or both of phosphorus and boron into the
6 material.

7 A characteristic of a deposited silicon oxide material is its so-
8 called flow temperature. A flow temperature is a temperature at which
9 the silicon oxide material will melt. Flow temperature can be an
10 important characteristic of silicon oxide materials. For instance,
11 incorporation of silicon oxide materials into semiconductor fabrication
12 processes frequently involves melting and reflowing of the materials to
13 increase planarity and obtain good coverage of the materials over
14 underlying device structures. Films consisting essentially of silicon
15 dioxide typically have flow temperatures of about $1,100^\circ\text{C}$ or higher.
16 Addition of boron or phosphorous to such films can reduce the flow
17 temperatures to less than 850°C . It would be desirable to further
18 reduce flow temperatures. Specifically, silicon oxide flow frequently
19 occurs after provision of semiconductor devices in a semiconductor
20 fabrication process. The high temperatures of silicon dioxide reflow can
21 adversely affect such devices.

22 Another characteristic of silicon oxide materials is density. Denser
23 materials generally have better flow properties than less dense materials.

Specifically, denser materials can frequently reflow over underlying nonplanar structures more quickly than can less dense silicon oxide materials. Accordingly, it would be desirable to develop methods for densifying silicon oxide materials.

SUMMARY OF THE INVENTION

In one aspect, the invention encompasses a method of forming an insulating material. A substrate is provided within a reaction chamber together with reactants comprising Si, F and ozone. An insulating material comprising fluorine, silicon and oxygen is deposited onto the substrate from the reactants.

In another aspect, the invention encompasses a method of forming a boron-doped silicon oxide having Si-F bonds. A substrate is provided within a reaction chamber together with reactants comprising F-TES, a boron-containing precursor, and ozone. A boron-doped silicon oxide having Si-F bonds is deposited onto the substrate from the reactants.

In yet another aspect, the invention encompasses a method of forming a phosphorus-doped silicon oxide having Si-F bonds. A substrate is provided within a reaction chamber together with reactants comprising F-TES, a phosphorus-containing precursor, and ozone. A phosphorus-doped silicon oxide having Si-F bonds is deposited onto the substrate from the reactants.

1 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

2 This disclosure of the invention is submitted in furtherance of the
3 constitutional purposes of the U.S. Patent Laws "to promote the
4 progress of science and useful arts" (Article 1, Section 8).

5 The invention encompasses methods of chemical vapor deposition
6 of insulating materials comprising fluorine, silicon and oxygen. In one
7 aspect, the invention encompasses a method wherein a substrate is
8 provided within a CVD reaction chamber together with reactants
9 comprising Si, F and ozone. Subsequently, an insulating material
10 comprising fluorine, silicon and oxygen is deposited onto the substrate
11 from the reactants.

12 In an exemplary embodiment of the invention, the Si and F are
13 comprised by a compound having an Si-F bond, such as, for example
14 F-TES (triethoxy fluorosilane). The F-TES is preferably flowed into the
15 reaction chamber at a rate from about 100 milligrams per
16 minute (mg/min) to about 500 mg/min. The ozone is preferably flowed
17 into the reaction chamber as a mixture with O₂ (the mixture preferably
18 containing from about 5% to about 15% ozone, by volume), with an
19 example being at a rate from about 1000 standard cubic centimeters per
20 minute (sccm) to about 5000 sccm, and preferably about 2000 sccm. In
21 addition to the F-TES and ozone, a second silicon precursor can be
22 flowed into the reaction chamber. Such second silicon precursor can
23 comprise, for example, TEOS. In alternative embodiments of the

invention, the Si reactants can comprise TEOS and the F reactants can be comprised by molecules lacking Si.

Temperature of the substrate within the reaction chamber is preferably maintained at from about 400°C to about 700°C, and more preferably maintained at about 500°C. Pressure within the reaction chamber is preferably maintained at from about 1 Torr to about 1 atmosphere, more preferably at from about ⁴⁰⁰~~500~~ Torr to about 1 atmosphere, and even more preferably at about ⁶⁰⁰~~400~~ Torr. Most preferably, no plasma is present within the CVD reaction chamber to reduce costs and process complexity. However, it is noted that the invention encompasses embodiments wherein plasma is present within the reaction chamber during the deposition process.

Under the above-described exemplary conditions, a material comprising fluorine, silicon and oxygen is deposited onto the substrate at a rate from about 500 Å/minute to about 10,000 Å/minute, and is typically deposited at a rate of about 8,000 Å/minute. The deposited material comprises silicon oxide interspersed with Si-F bonds. The fluorine is generally present in such material to a concentration from about 0.1 atomic percent to about 10 atomic percent.

An advantage of incorporating fluorine into a silicon oxide material is that the fluorine can reduce the flow temperature of the material. For instance, it is found that fluorine incorporation into a silicon oxide material to an amount of from about 0.1 atomic percent

1 to about 10 atomic percent can reduce a flow temperature of the
2 material. Specifically, it is found that a flow temperature of the
3 material can be reduced by from about 50°C to about 100°C relative
4 to a silicon oxide material that is identical to the fluorine-containing
5 material in all respects except for lacking the fluorine.

6 Another advantage of incorporating Si-F bonds into a silicon oxide
7 material (such as, for example, SiO₂ or borophosphosilicate glass) is that
8 the fluorine can decrease a dielectric constant of the material.

9 Yet another advantage of incorporating fluorine into a silicon
10 oxide material can be to reduce so-called fixed charge problems. Fixed
11 charges result when one or more silicon atoms are bonded to less than
12 four other atoms. In such circumstances, the silicon atoms can carry
13 positively-charged electron density and shift a threshold voltage of a
14 device incorporating the silicon atoms. Negatively charged fluorine
15 atoms can interact with the positively-charged electron density to
16 neutralize the density and alleviate fixed charge problems that would
17 otherwise occur.

18 It is noted that F-TES has been utilized in the prior art in CVD
19 processes for depositing silicon oxide materials. However, the F-TES
20 was not utilized in combination with ozone. An aspect of the present
21 invention is recognition that chemical vapor deposition of fluorine-
22 containing silicon oxide from reactants comprising F-TES can be
23 significantly improved if such reactants further comprise ozone.

Specifically, it is recognized that if the reactants comprise F-TES and lack ozone, very little fluorine is incorporated into a deposited silicon oxide. The advantageous effects of ozone have not been seen with other oxygen-containing precursors. Specifically, it is found that O_2 and/or H_2O_2 work significantly less well than ozone as co-reactants with F-TES. In other words, if a comparable concentration of H_2O_2 or O_2 is utilized under the above-described reaction conditions in substitution of ozone, the silicon oxide that is formed will have significantly less than 0.1 atomic percent fluorine incorporated therein. Such silicon dioxide will have higher flow temperatures and less density than a preferred silicon oxide formed according to a method of the present invention utilizing ozone in a chemical vapor deposition process. Also, H_2O_2 can be more difficult to work with than ozone. For instance, it can be more difficult to accurately control an H_2O_2 concentration in a reaction chamber than to control an ozone concentration in the chamber.

In other aspects of the invention, a fluorine-containing silicon oxide can be provided to be doped with, for example, one or both of phosphorous and boron. For instance, a phosphorous precursor can be incorporated as a reactant in a chemical vapor deposition process of the present invention to form an insulating material comprising fluorine, silicon, oxygen, and phosphorous. The phosphorous precursor can comprise, for example, TEPO. Preferably, the amount of phosphorous

1 incorporated into a fluorine-containing silicon oxide of the present
2 invention is from about 1 atomic percent to about 10 atomic percent.

3 Exemplary conditions for incorporating phosphorous into a
4 fluorine-containing silicon oxide utilizing a CVD process include:

5 a pressure within a CVD reaction chamber of from about 1 Torr
6 to about 1 atmosphere;

7 a temperature of a substrate within the chamber of from about
8 400°C to about 700°C;

9 a flow rate of F-TES into the reaction chamber of from about
10 100 mg/min to about 500 mg/min;

11 a flow rate of ozone-containing gas (provided as a mixture of
12 from about 5% to about 15% ozone in O₂) of from about 1000 sccm
13 to about 5000 sccm; and

14 a flow rate of TEPO in the reaction chamber of from about
15 25 mg/min to about 400 mg/min.

16 As another example, boron can be incorporated into a fluorine-
17 containing silicon oxide of the present invention by providing a boron-
18 containing precursor as a reactant in a CVD reaction chamber. The
19 boron-containing precursor can comprise, for example, TEB. The boron
20 is preferably provided in a fluorine-containing silicon oxide of the
21 present invention to a concentration of from about 1 atomic percent to
22 about 10 atomic percent, and more preferably provided to a
23 concentration of less than or equal to about 8 atomic percent.

1 An exemplary process for incorporating boron into a fluorine-
2 containing silicon oxide utilizing a CVD process includes:

3 a pressure within a CVD reaction chamber of from about 1 Torr
4 to about 1 atmosphere;

5 a temperature of a substrate within the chamber of from about
6 400°C to about 700°C;

7 a flow rate of F-TES into the reaction chamber of from about
8 100 mg/min to about 500 mg/min;

9 a flow rate of ozone-containing gas (provided as a mixture of
10 from about 5% to about 15% ozone in O₂) of from about 1000 sccm
11 to about 5000 sccm; and

12 a flow rate of TEB into the reaction chamber of from about
13 25 mg/min to about 400 mg/min.

14 In yet another exemplary application, a fluorine-containing silicon
15 oxide of the present invention can be provided to be doped with both
16 boron and phosphorous. Preferably, the boron and phosphorous atoms
17 are together provided to a concentration of from about 3 atomic percent
18 to about 12 atomic percent within the fluorine-containing silicon oxide.
19 An exemplary composition of the silicon oxide comprises about 3%
20 boron, about 7% phosphorous, and about 2% fluorine (by atomic
21 percent).

22 Exemplary conditions for forming the boron and phosphorous
23 doped fluorine-containing silicon oxide include:

1 a pressure within a CVD reaction chamber of from about 1 Torr
2 to about 1 atmosphere;

3 a temperature of a substrate within the chamber of from about
4 400°C to about 700°C;

5 a flow rate of F-TES into the reaction chamber of from about
6 100 mg/min to about 1000 mg/min;

7 a flow rate of ozone-containing gas (provided as a mixture of
8 from about 5% to about 15% ozone in O₂) of from about 1000 sccm
9 to about 8000 sccm;

10 a flow rate of TEPO in the reaction chamber of from about
11 25 mg/min to about 400 mg/min; and

12 a flow rate of TEB into the reaction chamber of from about
13 25 mg/min to about 400 mg/min. In preferred embodiments, the
14 pressure is from about 10 Torr to about 700 Torr.

15 In each of the above-described embodiments, the CVD reaction
16 chamber referred to is a single wafer, cold wall chamber. The invention
17 encompasses embodiment utilizing other types of reaction chambers.

18 In compliance with the statute, the invention has been described
19 in language more or less specific as to structural and methodical
20 features. It is to be understood, however, that the invention is not
21 limited to the specific features shown and described, since the means
22 herein disclosed comprise preferred forms of putting the invention into
23 effect. The invention is, therefore, claimed in any of its forms or

1 modifications within the proper scope of the appended claims
2 appropriately interpreted in accordance with the doctrine of equivalents.
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